

(12) UK Patent Application (19) GB (11) 2 260 340 (13) A
(43) Date of A publication 14.04.1993

(21) Application No 9221069.9

(22) Date of filing 07.10.1992

(30) Priority data

(31) 03264159

(32) 11.10.1991

(33) JP

(71) Applicant

Kabushiki Kaisha Kobe Seiko Sho

(Incorporated in Japan)

3-18 Wakinoama-cho, 1-chome, Chuo-ku, Kobe 651,
Japan

(72) Inventors

Kozo Nishimura

Koji Kobashi

Shigeaki Miyauchi

Rie Kato

Hisashi Koyama

Kimitsugu Saito

(74) Agent and/or Address for Service

Brookes & Martin

High Holborn House, 52-54 High Holborn, London,
WC1V 6SE, United Kingdom

(51) INT CL⁵

H01L 21/44, C01B 33/12, C23C 16/02 16/26 16/56

(52) UK CL (Edition L)

C7F FAXE FCD FHE FPCE FQ902 FR861 FR872
FR916 F103 F210 F242 F247 F284 F287 F304 F307
F310 F411 F412 F440 F802 F809

C1A AJ2

H1K KHAB K3U6A K4C23 K4C3S K4C5K K4F11G

K4F26 K8PC K9N3

U1S S2061

(56) Documents cited

GB 2252670 A EP 0458530 A2 EP 0209257 A1

EP 0086022 A1 DE 001544190 B

C.B.Child, Fourth Annual SD/ST-ONR Diamond
Technology Initiative Symposium, 1989

(58) Field of search

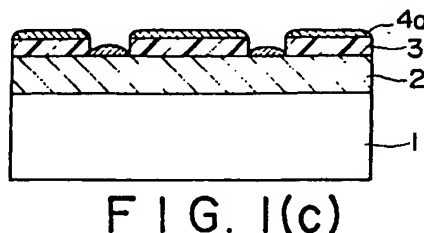
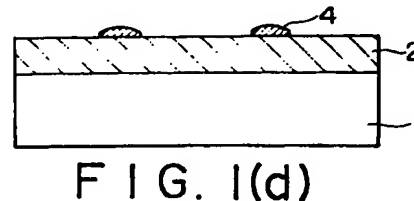
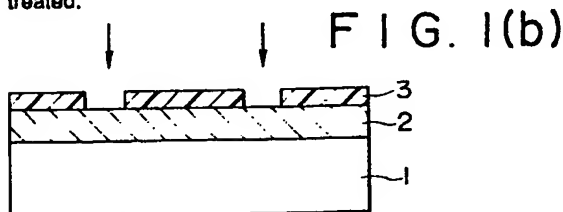
UK CL (Edition K) C7F FACE FACX FAXE FAXX
FCD FCF FHE FHZ FPCE FPCX FPDE FPD, H1K
KHAB

INT CL⁵ C23C, H01L

Online databases: WPI, CLAIMS

(54) Forming electrodes on diamond by plasma treating the diamond with inert gases

(57) A method of forming electrodes on diamond comprising the steps of forming a mask pattern on diamond (as a crystal) or diamond film deposited by CVD (Fig 1b); performing a treatment of the diamond surface by a plasma of chemically inert gases; forming an electrode film on the whole surface of the specimen (Fig 1c); and removing the mask, thereby forming a specified pattern on the electrodes (Fig 1d). This treatment of the diamond provides electrodes for electronic devices (eg heat sinks, diodes, transistors) having high adhesion to diamond and diamond film. The electrode pattern may be formed by a photolithography technique and may comprise a pattern of Au/Ti. The chemically inert gas may be He, Ne, Ar, Kr, Xe or N₂. During the plasma processing a bias voltage (DC or AC) may be applied to the sample holder to enhance the cleaning effect. In an example the chamber is evacuated to approximately 10⁻⁶ Torr and the inert gas is supplied at a flow rate of 10cc/min at a gas pressure of 2m Torr. After the step of forming the electrode the composite material may be heat treated.



1/2

FIG. 1(a)

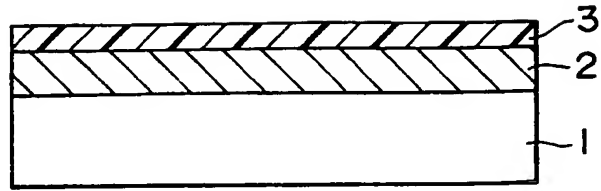


FIG. 1(b)

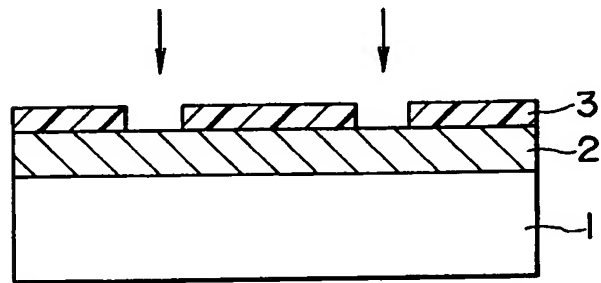


FIG. 1(c)

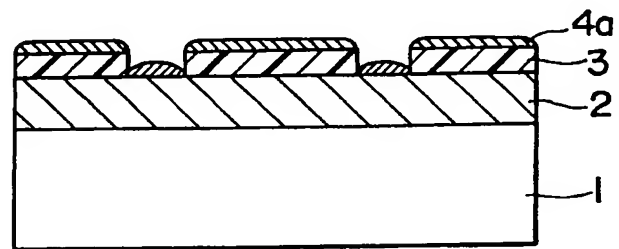
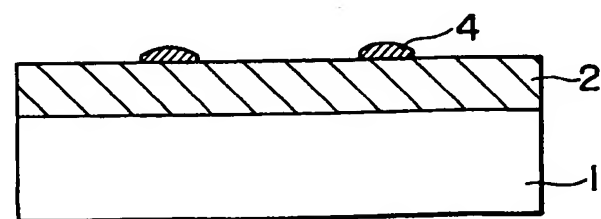
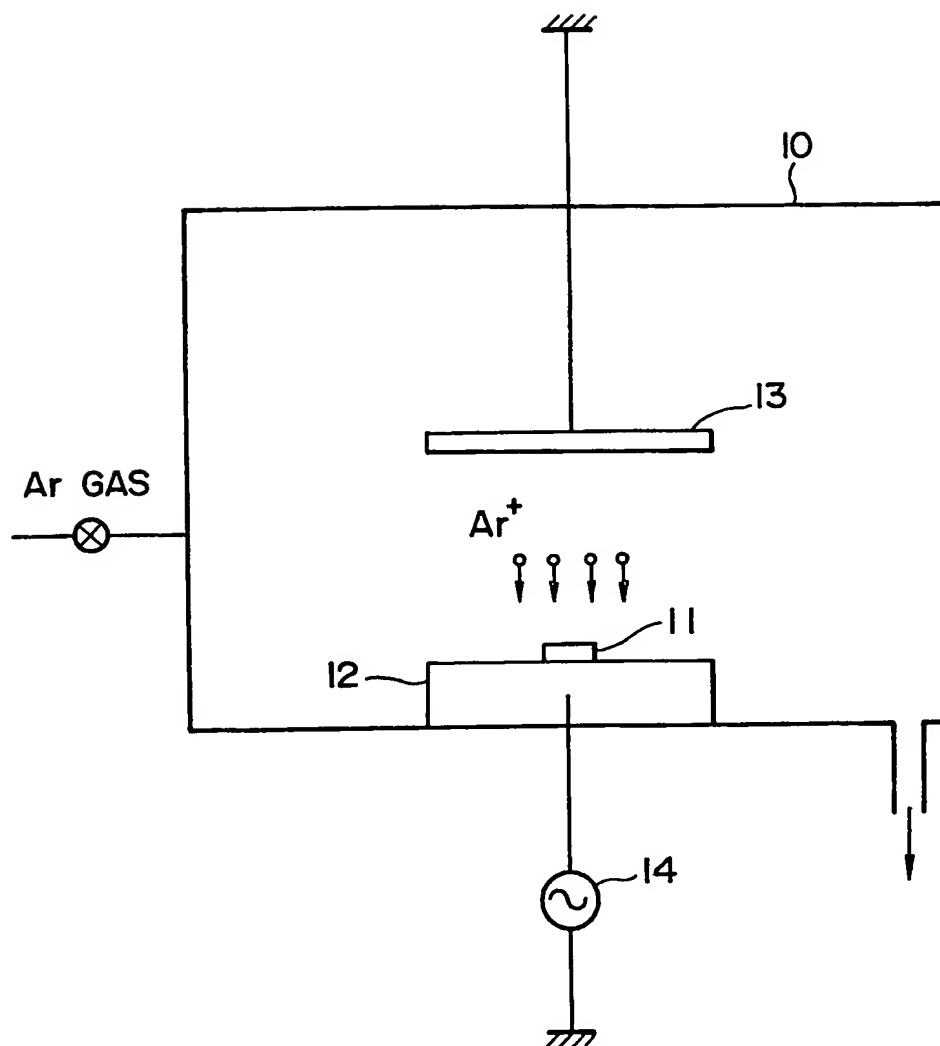


FIG. 1(d)



2/2

FIG. 2



METHOD FOR FORMING ELECTRODE ON DIAMOND
FOR ELECTRONIC DEVICES

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a method for forming electrodes with high adhesion to diamond for diamond electronic devices such as heat sinks, diodes, and transistors.

Description of the Related Art

Diamond has high hardness and stability against heat, radiation, and chemicals. It also has a large band gap of 5.4 eV. Diamond is electrically insulating, but becomes semiconducting by doping. Thus, diamond is expected to be used for electronic devices which can be operated at high temperatures. Furthermore, diamond is transparent over a wide wavelength range between ultraviolet and infrared, and is used for optical windows.

Diamond films formed by vapor deposition methods also have the above-mentioned excellent characteristics, and are used for coatings on cutting tools and speaker

diaphragms, as well as for electronic applications such as heat sinks, diodes, and transistors.

It is well known that diamond film can be formed by vapor phase synthesis using plasma chemical vapor deposition (CVD) at low cost. Similarly for bulk diamonds, synthesized diamond film becomes semiconducting by doping with an impurity such as boron (B).

In the fabrication of electronic devices using diamond, it is necessary to form electrodes on the surface of diamond. Known methods of forming electrodes on the surface of diamond are as follows:

(I) Ohmic contacts were obtained by a method of vapor-deposition of metals liable to form carbides, e.g. Ta, on diamond followed by a heat treatment by electron beam irradiation, thus forming a carbide intermediate layer at the interface between diamond and the metal electrode, thereby enhancing the adhesion [A.T. Collons et al. Formation of electrical contacts on insulating and semiconducting diamonds, Diamond Research, 1970]. This method will be referred to hereafter as Method I.

(II) Ohmic contacts were obtained by a method of vapor-deposition of metals liable to form a carbide, e.g. Mo, on diamond followed by a heat treatment using a

vacuum furnace [K.L. Moazed et al. Material Research Society Symposium Proceedings 162, P.347, 1990).

Using this method, electrodes with high adhesion were formed by heat-treating metal films having multiple layer structures such as Au/Pt/Ti, Au/Ti, or the like. This method will be referred to hereafter as Method II.

(III) Metal electrodes were formed after irradiating Ar ions on the surface of diamond, thereby transforming the surface thereof into graphite [C.B. Child, Fourth Annual SD 10/IST-ONR Diamond Technology Initiative Symposium, 1989]. By this method, Au electrodes with high adhesion were formed on the surface of diamond. This method will be referred to hereafter as Method III.

However, the above-described methods have the following problems:

In Method I, it is necessary to perform the heat treatment using an electron beam generator at high vacuum, which is expensive and time consuming. Thus, this method is disadvantageous in terms of production cost.

In Method II, the metal electrodes which have been vapor-deposited on diamond must be heated at high temperature (e.g. 800°C) to form a carbide. This causes

a stress at the interface between the electrode and the diamond due to the difference in thermal expansion coefficients. Thus, this method has the disadvantage that the electrodes are thermally damaged and tend to peel off from the diamond.

Also, in a heat treatment at high temperatures, the surface of a diamond is transformed into graphite. Thus, in this method, low resistance parasitic channels are liable to be formed on the surface of a diamond. Furthermore, similarly for Method I, since this method employs a vacuum furnace in the heat treatment, this process is very time consuming.

In Method III, an expensive ion beam generator has to be operated at high vacuum, which is costly and time consuming. Furthermore, when a processed sample is subjected to ultrasonic cleaning, the electrodes partially or totally peel off because of poor adhesion.

SUMMARY OF THE INVENTION

An objective of the present invention is to provide a method for forming electrodes with high adhesion to diamond for electronic device fabrication.

To achieve the objective, in a preferred mode of the present invention, there is provided a method for

forming electrodes on electronic devices using diamond comprising the steps of: first performing a plasma treatment on the surface areas of a diamond where electrodes are to be formed by a plasma of inert gases, and then depositing electrode materials on the surface areas of the diamond.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other objectives, features, and advantages of the present invention will become more apparent from the following description taken in connection with the accompanying drawings, in which:

Figures 1a to 1d are cross-sectional views showing a method for forming electrodes on a diamond film formed on a substrate, according to the first example of the present invention (Note that when bulk diamonds are used, substrate 1 in Figs. 1a-1d is unnecessary.); and

Figure 2 is a typical view showing a magnetron sputtering apparatus.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Prior to the description of the preferred embodiments, the function of the present invention will be explained.

The present applicants have found that a high adhesion of electrodes to diamond can be obtained by performing a plasma treatment of a diamond surface where the electrodes are to be formed, by a plasma of inert gases. By this treatment, hydrocarbon, water, and the like adhering on a diamond surface are removed by exposing the surface to the plasma, with the adhesion of the electrodes to the diamond surface becoming very high.

This invention can be employed not only for bulk diamond crystals, but also for diamond films synthesized by CVD.

Also, by this treatment, a very thin surface layer of a diamond surface area is transformed into graphite by the damage due to plasma exposure. This contributes to the improvement of the adhesion of the electrodes to the diamond surface, because the adhesion of metal films to graphite is generally better than that of metal films to diamond.

The above-mentioned inert gases include rare gases such as He, Ne, Ar, Kr, or Xe, or chemically inert gases such as N₂. During the plasma processing, a bias voltage, either direct or alternating current (DC or

AC), may be applied on the sample holder to enhance the cleaning effect.

When a metal liable to form a carbide is used for an electrode on a diamond surface, which is then followed by a heat treatment under suitable conditions, a carbide layer is formed by the reaction between the metal electrodes and diamond, thus enhancing the adhesion of the electrode to diamond. This also creates electronic defect levels at the interface, which contribute to the ohmic nature of the contact.

Furthermore, diffusion of electrode materials occurs by a heat treatment, which also results in defect levels at the interface between the electrodes and diamond. Consequently, the ohmic electrodes are liable to be formed.

The temperature and duration of the heat treatment are dependent on the kinds of electrode material: for the case of Au/Ti, a heat treatment can be done at 400°C for one hour.

Finally, and technologically more importantly, the process invented here, namely, the plasma treatment of a diamond surface followed by electrode formation, can be done in the same vacuum chamber for sputtering, for instance, as explained later in Examples 1-3.

Therefore, there is no loss of time in the device fabrication process nor need for extra costly apparatus. Moreover, the present invention can be employed not only for bare diamond surfaces, but also for diamond surfaces photolithographically patterned by such mask materials as photoresist, metals, or ceramic films without damaging the mask materials during the plasma treatment under proper conditions.

The present invention will be more apparent by way of the following examples with reference to the accompanying drawings.

Example 1

Figures 1a to 1d are cross-sectional views showing a method of forming electrodes according to this example of the present invention in the order of fabrication processes when the electrodes are formed on a diamond film 2. However, note that no substrate is necessary when electrodes are formed on bulk diamond crystals.

Figure 2 is a view of a standard magnetron sputtering apparatus used for the plasma treatment of the diamond surface. In Fig. 2, a sample 11 (consisting of a diamond film and a photoresist film) was mounted on a sample stage 12 in a vacuum chamber 10. The electrode

13 was grounded, and high frequency voltage was applied from an RF power supply 14 to the sample stage 12 to generate a plasma. The sample 11 was thus surface-treated by the plasma. In the above, the chamber 10 was evacuated to approximately 10^{-6} Torr, and then an inert gas (or a mixture of inert gases) was fed at the flow rate of 10 cc/min at a gas pressure of 2 mTorr into the chamber 10. The frequency of a power supply 14 was 13.56 MHz, the RF output was 100 W, and the plasma treatment time was 1 min.

In this example, the experiments were done in the following procedure:

(1) First, as shown in Fig. 1, a semiconducting diamond film 2 was formed on a substrate 1 to a thickness of approximately 2 μm by microwave plasma CVD. As a reaction gas for diamond film deposition, CH_4 was diluted by H_2 (concentration: 0.5%), and a doping gas of B_2H_6 (concentration: 0.01ppm) was added. During the CVD, the substrate temperature was maintained at 800°C , and the gas pressure in the reaction chamber was 35 Torr. The CVD was continued for 7 hours. The diamond film 2 thus obtained was then coated with a photoresist film 3 using the standard photolithography technique.

(2) As shown in Fig. 1b, openings according to the specified electrode pattern were formed on the photoresist film 3 using a photolithography technique. The specimen was then placed in the above-mentioned sputtering apparatus (Fig. 2), and plasma-treated using the conditions described above. As a result, only the surface area of the diamond film 2 were treated by a plasma through the openings.

(3) The metal electrodes were formed using the same magnetron sputtering apparatus as shown in Fig. 1c. In this case, a target of electrode material was placed on the electrode 13, and a DC bias voltage was applied on the target side. The substrate side was grounded so that an electrode film 4a of a bilayer structure, made of a Ti film and an Au film, was formed on the whole surface of the substrate. The formation conditions of the Ti film and the Au film are shown in Table 1.

Table 1

	Ti film	Au film
DC discharge condition	0.8 A, 390 V	0.2 A, 535 V
film deposition time	15 sec.	1 min.
film thickness	400 Å	2000 Å

(4) As shown in Fig. 1d, the photoresist film 3 was removed together with the electrode film 4a on the photoresist film 3. Thus, a pattern of Au/Ti electrodes 4 was obtained.

The sample thus obtained was subjected to ultrasonic cleaning using pure water for 8 min., but the electrodes did not peel off. As a comparative example, a sample obtained by forming electrodes without the surface treatment by plasma was subjected to ultrasonic cleaning in the same conditions as in this example. However, more than 90% of the electrode pattern peeled off after approximately 10 sec.

Example 2

A similar experiment as in Example 1 was carried out. Here, an SiO_2 film was deposited on a diamond film by magnetron sputtering in place of the photoresist film of Example 1, and the openings were formed on the SiO_2 film according to a predetermined pattern by etching using a photolithography technique. Au/Ti electrodes were then deposited on the surface of the sample. The sample thus obtained was subjected to the ultrasonic cleaning in the same condition as in Example 1. However, no electrodes peeled off.

In the surface treatment using the inert gas plasma in Examples 1 and 2, the RF output applied to the electrode 11 was changed. When the RF output was 600 W, the electrode pattern formed by the photoresist film was severely damaged, which made it impossible to form the electrodes by the lift-off method. Therefore, when a high RF output was required, an SiO_2 film was preferably used in place of the photoresist film as a mask material.

Example 3

The experiment was repeated in a similar manner as in Examples 1 and 2. In this case, the heat treatment was done after the plasma treatment and the electrode formation, under the condition of a temperature of 400°C , a pressure of 10^{-6} Torr, and a processing time of 30 min. The sample was then subjected to an ultrasonic cleaning in the same conditions as described in Example 1. However, no separation of the electrodes was found. In this example, the contact resistance between each metal electrode and the diamond film was reduced by approximately 2 orders of magnitude as compared with the cases without heat treatment.

CLAIMS

1. A method of forming an electrode on diamond comprising the steps of:

treating the diamond surface on which said electrode is to be formed using a plasma of a chemically inert gas or a mixture of chemically inert gases; and

forming said electrode on said surface.

2. A method of forming an electrode on diamond according to claim 1, wherein said method further comprises the step of performing a heat treatment after the step of forming said electrode.

3. A method of forming an electrode on diamond according to claim 1 or 2, wherein an electrode pattern is formed using a photolithography technique.

4. A method of forming an electrode on diamond according to claims 1 to 3, wherein said diamond is a natural or a synthetic bulk diamond or a diamond film formed by vapor-deposition methods.

5. A method according to any one of the preceding claims wherein bias voltage is applied to a support for the diamond surface during said treatment.

6. A method according to any one of the preceding claims wherein the treatment of the diamond surface is carried out in a magnetron sputtering apparatus and the

electrode is formed on the treated diamond surface by vapour deposition the same apparatus.

Patents Act 1977
Examiner's report to the Comptroller under
Section 17 (The Search Report)

Application number

GB 9221069.9

Relevant Technical fields

(i) UK Cl (Edition K) C7F (FACE, FACX, FAXE, FAXX,
 FCD, FCF, FHE, FHZ, FPCE, FPCK
 FPDE, FPDY); H1K (KHAB)
 (ii) Int Cl (Edition 5) C23C; H01L

Search Examiner

P G BEDDOE

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI, CLAIMS

Date of Search

12 NOVEMBER 1992

Documents considered relevant following a search in respect of claims

1-6

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2252670 A (KABUSHIKI) - see especially Claim 1 and Examples	1,3,4
X,P	EP 0458530 A2 (SUMITOMO) - 27 November 1991 see especially Claim 1 and embodiments 1 and 2	1,3,4,5
X	EP 0209257 A1 (DE BEERS) - see especially page 10 lines 19-30	1,4
X	EP 0086022 A1 (N V OPTISCHE) - see especially page 3 line 15 - page 4 line 30	1, 4
X	DE 1544190 B (GEC) - see english language abstract (WPI Accession No: 74-05745V/04)	1, 4
X	C B Child, Fourth Annual SD/IST-ONR Diamond Technology Symposium, 1989	1, 4

Category	Identity of document and relevant passages	Relevant to claim(s).

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINE OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.